

A re-evaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the ocean

Jickells, T.D.¹, Buitenhuis¹, E., Altieri, K.², Baker, A.R.¹, Capone, D.³, Duce, R.A.⁴, Dentener, F.⁵, Fennel, K.⁶, Kanakidou, M.⁷, LaRoche, J.⁸, Lee, K.⁹, Liss, P.¹, Middelburg, J. J.¹⁰, Moore, J.K.¹¹, Okin, G.¹², Oschlies, A.¹³, Sarin, M.¹⁴, Seitzinger, S.¹⁵, Sharples, J.¹⁶, Singh, A.¹⁴, Suntharalingam, P.¹, Uematsu, M.¹⁷, Zamora, L.M.¹⁸

1. School of Environmental Science University of East Anglia UK
2. Energy Research Centre University of Cape Town SA
3. Department of Biological Sciences University of S California USA
4. Departments of Oceanography and Atmospheric Sciences Texas A&M University USA
5. European Commission, DG Joint Research centre, Ispra Italy
6. Department of Oceanography Dalhousie University Canada
7. Department of Chemistry, University of Crete, Greece
8. Department of Biology Dalhousie University, Canada
9. School of Environmental Science and Engineering, Pohang University of Science and Technology, Republic of Korea.
10. Faculty of Geosciences University of Utrecht Netherlands
11. Department of Earth System Science University of California at Irvine USA
12. Department of Geography University of California USA
13. GEOMAR Kiel Germany
14. Geosciences Division at Physical Research Laboratory, Ahmedabad, India
15. Department of Environmental Studies, University of Victoria, Canada
16. School of Environmental Sciences, U Liverpool UK
17. Center for International Collaboration, Atmosphere and Ocean Research Institute, The University of Tokyo Japan
18. NASA Goddard Space Flight Centre, Greenbelt, MD, USA and Universities Space Research Centre, MD, USA.

Key Points

- A new estimate of total atmospheric fixed nitrogen inputs to the ocean (39 Tg N yr^{-1}) and its spatial distribution is presented and compared to estimates of inputs from other sources.
- The effects of atmospheric deposition on the oceans are estimated as an increase of productivity equivalent to an uptake of $0.15 \text{ Pg C yr}^{-1}$.
- Four key uncertainties that need to be resolved to improve estimates of the impacts of nitrogen deposition on the oceans are identified.

Abstract

We report a new synthesis of best estimates of the inputs of fixed nitrogen to the world ocean via atmospheric deposition, and compare this to fluvial inputs and di-nitrogen fixation. We evaluate the scale of human perturbation of these fluxes. Fluvial inputs dominate inputs to the continental shelf, and we estimate about 75% of this fluvial nitrogen escapes from the shelf to the open ocean.

Biological di-nitrogen fixation is the main external source of nitrogen to the open ocean, i.e. beyond the continental shelf. Atmospheric deposition is the primary mechanism by which land based nitrogen inputs, and hence human perturbations of the nitrogen cycle, reach the open ocean. We estimate that anthropogenic inputs are currently leading to an increase in overall ocean carbon sequestration of $\sim 0.4\%$ (equivalent to an uptake of $0.15 \text{ Pg C yr}^{-1}$ and less than the Duce et al., 2008 estimate). The resulting reduction in climate change forcing from this ocean CO_2 uptake is offset to a small extent by an increase in ocean N_2O emissions. We identify four important feedbacks in the ocean atmosphere nitrogen system that need to be better quantified to improve our understanding of the perturbation of ocean biogeochemistry by atmospheric nitrogen inputs. These feedbacks are recycling of (1) ammonia and (2) organic nitrogen from the ocean to the atmosphere and back, (3) the suppression of nitrogen fixation by increased nitrogen concentrations in surface waters from atmospheric deposition, and (4) increased loss of nitrogen from the ocean by denitrification due to increased productivity stimulated by atmospheric inputs.

Introduction

Oceanic biogeochemical cycles play many important roles in the Earth system, including sustaining marine productivity by the cycling of carbon and the key nutrients N, P, Si and Fe [P. Falkowski *et al.*, 1998; P. Falkowski *et al.*, 2000]. Marine productivity in turn affects air-sea gas exchange of greenhouse gases and thereby planetary radiative balance and climate. The oceans represent a very large planetary reservoir of fixed or reactive nitrogen i.e. nitrogen that is in forms other than the unreactive gaseous N_2 . Henceforth fixed nitrogen will be simplified to “nitrogen”, and when we specifically include dinitrogen gas, N_2 , this will be stated. The internal cycling of this nitrogen within the oceans, predominantly as nitrate in deep water, supports much of the primary production in the surface ocean on annual to decadal timescales. External inputs of nitrogen to the oceans from rivers, groundwater and direct waste discharges, atmospheric deposition and oceanic di-nitrogen (N_2) fixation (henceforth nitrogen fixation) may further augment ocean productivity. These inputs, together with those of other key potentially limiting nutrients such as P and Fe [Krishnamurthy *et al.*, 2010; C M Moore *et al.*, 2013; Okin *et al.*, 2011], regulate the long- term biological productivity of the ocean and hence ocean carbon storage.

Prior to human intervention, we assume a steady state for the ocean nitrogen budget in which external inputs should balance losses. These losses occur primarily by denitrification and anaerobic ammonia oxidation or anammox (subsequently simplified to denitrification in the text). The nitrate ocean residence time is <3000 years [Voss *et al.*, 2013][Bianchi *et al.*, 2012; Gruber and Galloway, 2008; Landolfi *et al.*, 2015]

The global nitrogen cycle is now being massively perturbed by human activity, particularly on land, and this affects the coastal oceans [Fowler *et al.*, 2013; Gruber and Galloway, 2008; Rockstrom *et al.*, 2009]. Although exact budgets are uncertain, estimated anthropogenic release of nitrogen into the global environment (160 Tg N yr^{-1} , $\text{Tg} = 10^{12}\text{g}$) is now of similar magnitude to all natural nitrogen fixation (250 Tg N yr^{-1}), and may increase in the future with a growing global population, depending

on societal progress in limiting nitrogen fluxes [Gruber and Galloway, 2008]. The increasing inputs of nitrogen from human activity, predominantly from land based activities, have the potential to modify oceanic, and even global, biogeochemical systems. However, our understanding of the scale and impact of such perturbations on the oceans is even less complete than on land [Fowler *et al.*, 2013; Gruber and Galloway, 2008].

Duce *et al.* [2008], Suntharalingam *et al.* [2012], Yang and Gruber [2016] and Krishnamurthy *et al.* [2007] have recently provided estimates of atmospheric inputs of fixed nitrogen to the world oceans and the impact of this deposition on ocean biogeochemistry. Duce *et al.*, [2008] also argued that atmospheric deposition is the dominant mechanism by which anthropogenic perturbations of the nitrogen cycle affect the open ocean, because of effective removal of fluvial nitrogen inputs on shelves by denitrification. Recognising that there has been considerable new information on atmospheric emissions and their deposition to the oceans, as well as improved modelling capability of their impacts since the publication of Duce *et al.* [2008], many of the authors of that paper have come together to re-evaluate their earlier conclusions. In this contribution we therefore update the Duce *et al.* [2008] study, reporting improved estimates of the preindustrial and modern atmospheric nitrogen inputs to the ocean. We also report improved models to describe the distribution and impact of these inputs on the oceans and their impacts on the exchange of some important greenhouse gases. We also consider possible future changes in the nitrogen fluxes. In addition we reconsider the assumption in the Duce *et al.* paper that fluvial nitrogen is completely removed by denitrification on shelves, and hence does not affect the nitrogen budget of the open oceans.

We begin by considering the three main external nitrogen sources to the oceans, fluvial, atmospheric and biological nitrogen fixation, before moving on to consider the impacts of changing atmospheric nitrogen inputs on ocean biogeochemistry. As shown in earlier work [Duce *et al.*, 2008] nitrogen fixation by lightning is quantitatively a very small component of the global nitrogen cycle

compared to other inputs: $\sim 5 \text{ Tg N yr}^{-1}$ [Fowler *et al.*, 2013]. It is included in the models here and is assumed to be unaffected by human activity, and hence not explicitly discussed further.

Fluvial Inputs to the oceans

Freshwater nitrogen inputs to the world oceans include riverine and submarine groundwater inputs plus some direct discharges. River inputs dominate and hence are our focus here [T. D. Jickells and Weston, 2011]. Riverine nitrogen fluxes at the freshwater/saltwater boundary have now been modeled and validated against available data, with associated uncertainty, [S. P. Seitzinger *et al.*, 2005; S. P. Seitzinger *et al.*, 2010]. These authors report a global flux estimate of 23 Tg N yr^{-1} for dissolved inorganic nitrogen (DIN) and 11 Tg N yr^{-1} for dissolved organic nitrogen (DON). The total river input of nitrogen to the coastal seas has approximately doubled over the last few hundred years [Beusen *et al.*, 2016; C M Moore *et al.*, 2013; S. P. Seitzinger *et al.*, 2010]. This input is also now dominated by nitrate, although in preindustrial times organic N may have made a much higher relative contribution [T. D. Jickells and Weston, 2011; S. P. Seitzinger *et al.*, 2005]. The general agreement between independent estimates [Beusen *et al.*, 2016; S. P. Seitzinger *et al.*, 2010] provides confidence in the estimated fluvial N fluxes. The validation, calibration and bias evaluations of the models' estimates are discussed in the individual papers.

Models and field data have suggested that much of the riverine nitrogen input is consumed on continental shelves, primarily by sediment denitrification fueled by organic carbon derived from shelf sea primary production [Duce *et al.*, 2008; Fennel *et al.*, 2006; S.P. Seitzinger *et al.*, 2006]. This leads to the suggestion that shelf seas are a global ocean nitrogen sink, rather than a source to the open ocean. The significance of this shelf sea fluvial nitrogen sink is however uncertain and depends, at least in part, on the water residence time on the shelf and how and where the open ocean/shelf sea boundaries are placed. We next consider how much of the nitrogen delivered by rivers reaches

the open ocean, and how much is utilized and denitrified on the shelf based on Sharples et al. [2016].

Fluvial particulate organic nitrogen (along with other fluvial particulate matter) is effectively trapped in estuaries at low salinity by particle flocculation [e.g. *Slattery and Phillips*, 2011] or on the shelf [*Muller-Karger et al.*, 2005]. However, it may be subsequently degraded to dissolved forms of nitrogen and thereby escape this particulate matter trap.

The main mechanism for long-term trapping of fluvial dissolved inorganic nitrogen on the shelf is the microbial consumption of nitrate by denitrification in shelf sediments [*Voss et al.*, 2013]. The effectiveness of shelf sea fluvial nitrate retention is then a function of both the rates of shelf sedimentary denitrification, and the residence time of water on the shelf [*S.P. Seitzinger et al.*, 2006]. The residence time of fluvial water on the shelf is not well known, but can be anticipated to be very variable, being influenced by the width of the shelf, flow rates within the coastal buoyant plumes and the net rates of water exchange across the shelf break. At a global scale, a key influence on circulation is the Coriolis force which acts to turn freshwater plumes to the right in the northern hemisphere, and to the left in the southern hemisphere, as the buoyant water exits the estuary. This tends to retain the estuary discharge within the shelf sea, inhibiting the freshwater and associated nitrogen from directly crossing the shelf. This increases the water residence time on the shelf. The Coriolis force is highly dependent on latitude, and the analysis of Sharples et al [2016] suggests that only near the equator (within about 20° latitude) is the Coriolis force weak enough to allow direct across-shelf movement of river plumes. Elsewhere the Coriolis force moves freshwater flows along shelf. This creates freshwater residence times on the shelf that are sufficiently long (months to years) to allow effective removal of most riverine nitrogen, although slowly degrading riverine DON will be exported [*Fennel et al.*, 2006; *Letscher et al.*, 2013; *Sharples et al.*, 2016].

The limited influence of the Coriolis force near the equator means that the residence time of the freshwater on the shelf there may be sufficiently short (days to weeks) that freshwater inputs will

rapidly cross the shelf to reach the open ocean and hence there may not be time for fluvial dissolved nitrogen inputs to be denitrified. By contrast at higher latitudes the residence times of river water on shelf are increased by the Coriolis force to the point (many months or longer) where sediment denitrification can utilize effectively all of the riverine nitrogen input [Sharples *et al.*, 2016].

The rivers discharging in tropical equatorial region include many with high flows per unit catchment area, due to high rainfall [Syvitski *et al.*, 2005], and many with globally important total water flows such as the Amazon, Zaire and Fly. These rivers may also have relatively low inorganic nitrogen concentrations, because of both less intensive catchment agriculture and dilution of nitrogen inputs by the high river flow. However, these rivers still deliver important total nitrogen loads due to the high water flows [S. P. Seitzinger *et al.*, 2005; S. P. Seitzinger *et al.*, 2010]. Dissolved organic nitrogen (DON) is often a significant component of the total dissolved nitrogen flux in these tropical river systems [T. D. Jickells and Weston, 2011; S. P. Seitzinger *et al.*, 2005]. This material contains a complex mixture of compounds and the rate of degradation of these DON components is very poorly known [Hansell, 2013]. Assuming the relatively biogeochemically labile DON is degraded on a timescale of about 50 days [Lønborg and Álvarez-Salgado, 2012] then such biologically labile DON may escape across the shelf to the open ocean from low latitude equatorial rivers due again to the shorter shelf residence times of freshwater in these systems. At high latitudes the labile DON may be degraded on the shelf and will then be retained along with nitrate on the shelf. More slowly degraded DON may be transported to the open ocean [Letscher *et al.*, 2013; Letscher *et al.*, 2015].

Sharples *et al.* [2016] estimate that net global fluvial dissolved inorganic nitrogen (DIN) inputs across the shelf break to the open ocean are about $17 \pm 4 \text{ Tg N yr}^{-1}$. This implies that globally about 75% of fluvial DIN is transported across the shelf to the oceans with the main inputs occurring near the equator (Figure 1). This DIN flux will be augmented by a riverine DON flux (11 Tg N yr^{-1}), although the uncertainties in our understanding of the composition and reactivity of this material mean we cannot estimate the shelf wide retention of this flux with any confidence. These fluxes contrast to

the Duce et al. [2008] assumption of complete nitrogen retention on the shelf. The Sharples et al [2016] flux estimation excludes estuarine nitrogen retention, and thus is an upper limit on nitrogen inputs to the open ocean.

As noted earlier global fluvial nitrogen fluxes to the oceans have probably doubled since 1860 [Beusen et al., 2016; C M Moore et al., 2013]. Seitzinger et al. [2010] suggest that riverine fluxes of nitrogen may increase by -3 to +10% by 2030, depending on the assumed development scenario. Hence the overall eutrophication pressures on coastal systems from nitrogen loading are likely to continue. An important control on shelf nutrient retention is associated with physical oceanographic factors particularly the Coriolis force, and we suggest the spatial distribution of fluvial inputs, and hence the physical controls on the effectiveness of shelf retention of these inputs, is likely to remain similar between 2005 and 2030. Thus the overall changes in the fluvial nitrogen fluxes to the open ocean are likely to be small, although locally large changes in Arctic regions may follow from global warming.

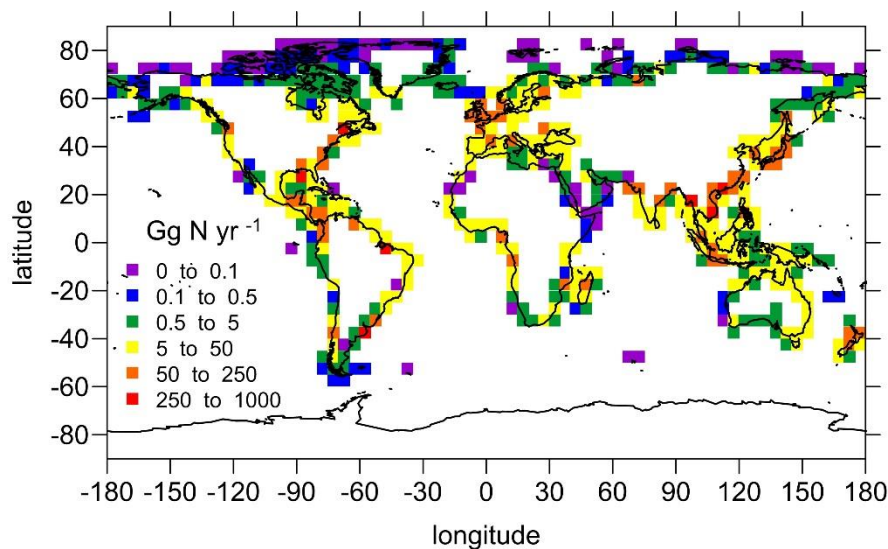


Figure 1. N supply across shelf and to the open ocean in 5°x5° boxes based on NEWS river inputs [S. P. Seitzinger et al., 2010] and shelf retention estimates [Sharples et al., 2016] illustrating the dominance of tropical rivers as nitrogen sources capable of transporting nitrogen across the shelf to the open ocean [Sharples et al., 2016].

Biological Nitrogen Fixation

Biological nitrogen (N_2) fixation offers the marine phytoplankton community a mechanism to relieve nitrogen limitation. However, biochemical mechanisms for nitrogen fixation require considerable energy expenditure. Biological nitrogen fixation also requires relatively large amounts of iron [Grosskopf and LaRoche, 2012; Kustka et al., 2003]. Nitrogen fixation is restricted to a small group of prokaryotic planktonic organisms, although evidence from genetic studies suggests the range of organisms able to fix nitrogen may be greater than previously thought [Bombar et al., 2016]. Estimates of global nitrogen fixation rates and controls are very uncertain [Landolfi et al., 2015; Mahaffey et al., 2005; C. J. Somes and Oschlies, 2015; C. J. Somes et al., 2013]. At regional and basin scales nitrogen fixation rates can be estimated using direct measurements, abundance estimates of nitrogen fixers and from estimates of nitrogen abundance relative to phosphorus, N^* [e.g. Singh et al., 2013]. However, at a global scale, estimates of nitrogen fixation rates have been derived from three different approaches; (1) plankton biogeochemical models constrained by marine chemistry data [e.g. Benavides et al., 2013; Mills and Arrigo, 2010], (2) from self-assembling ecosystem models, which do not prescribe biological rates directly but derive them to achieve the best fit to geochemical data [Dutkiewicz et al., 2012] and (3) from extrapolations of direct measurements of biological nitrogen fixation [e.g. Grosskopf et al., 2012]. Some recent studies have reported methodological issues that may cause earlier direct measurements of nitrogen fixation rates to be inaccurate [Dabundo et al., 2014; Grosskopf et al., 2012].

The most recent direct measurement based estimates of global ocean nitrogen fixations rate is about 177 TgN yr^{-1} [Grosskopf et al., 2012]. The self-assembly ecosystem models estimate nitrogen fixation rates to be 85 TgN^{-1} (range 66-135) [Dutkiewicz et al., 2012], while other recent model estimates range from $91\text{-}137 \text{ TgN yr}^{-1}$ [Bianchi et al., 2012; Landolfi et al., 2015] The PlankTOM model used here to assess the impacts of atmospheric deposition on the oceans [Buitenhuis et al., 2013; Le Quere et al., 2005] estimates global ocean nitrogen fixation rates of 164 TgN yr^{-1} (Figure 2),

broadly consistent with these other estimates and somewhat higher than, but within the uncertainties of, the estimate of 100 (60-200) Tg N yr⁻¹ used in Duce et al. [2008]. Nitrogen fixation rates are high in warm tropical oligotrophic waters and where there is sufficient availability of water column P and Fe [Luo et al., 2012; C. J. Somes and Oschlies, 2015]. The model results (Figure 2) also predict high nitrogen fixation in some coastal areas in S E Asia, which probably reflects stimulation by riverine phosphorus inputs. The global models are rarely able to fully capture the complex and episodic nature of nitrogen fixation blooms, and we note for example that high rates of nitrogen fixation have been observed in the Arabian Sea [Gandhi et al., 2011].

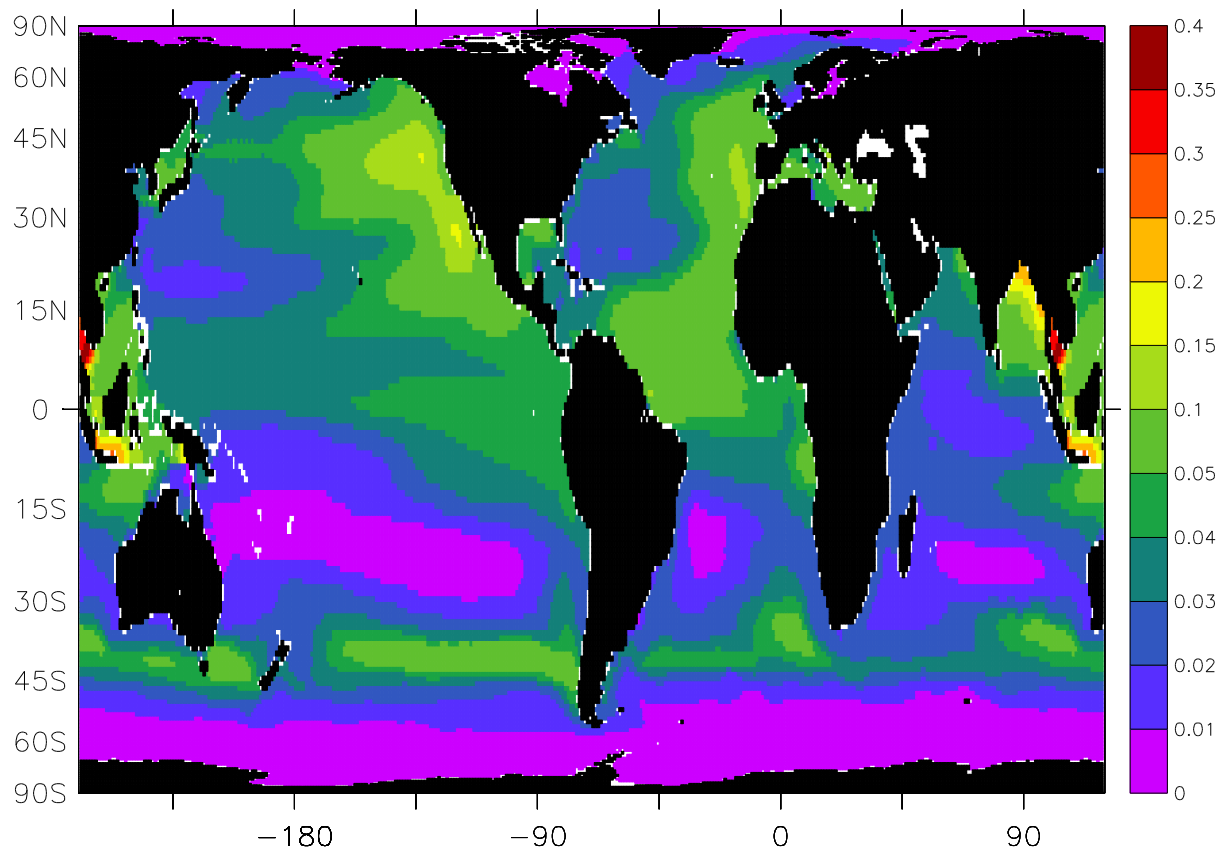


Figure 2. Nitrogen Fixation Rate estimates from PlankTOM model (see text) as molNm⁻²yr⁻¹, averaged over the period 1990-1999.

Based on current estimates [*Bianchi et al.*, 2012] of nitrogen loss from the ocean by burial and denitrification (260 Tg N yr⁻¹), only at the high end of this range of estimated nitrogen fixation rates is the ocean nitrogen cycle balanced. This has led to a discussion of whether the pre-industrial ocean nitrogen system is in steady state or not after recovery from glaciation and the restoration of the current continental shelves [*Bianchi et al.*, 2012; *Codispoti*, 2007; *Grosskopf et al.*, 2012; *C. J. Somes et al.*, 2013]. The usual biogeochemical assumption of ocean steady state may be inappropriate if the oceanic nitrogen system is still responding to postglacial maximum sea level rise when there was little or no continental shelf, and hence the ocean nitrogen cycle may have been very different. The nitrogen isotopic composition record of organic matter preserved in foraminifera within ocean sediments does suggest a major reorganisation of the oceanic nitrogen cycle between glacial and interglacial conditions [*Straub et al.*, 2013]. In regions like the Arabian Sea oxygen depleted zones, denitrification has been shown to fluctuate on even shorter (century) time scales. [*Altabet et al.*, 2002; *Suthhof et al.*, 2001], due to regional changes in environmental conditions. However, with nitrogen fixation and other input and removal rates of the order proposed above, and assuming steady state, the ocean residence time of nitrogen becomes short enough (of the order of 3000 years) that post glacial maximum re-equilibration should have been achieved [*C. J. Somes et al.*, 2013]. Hence a pre-anthropocene steady state should apply. The oceanic residence times of N and phosphorus (P) are therefore quite distinctly different, despite their close ocean scale coupling as is evident from the Redfield ratio. This coupling is due to large scale thermohaline water mixing that smooths out the effects of the different internal ocean biogeochemical N and P cycling [*Martiny et al.*, 2013; *Singh et al.*, 2015; *T S Weber and Deutsch*, 2010]

Nitrogen fixation in the oceans is controlled in part by the availability of P and Fe [*Ito et al.*, 2016; *C M Moore et al.*, 2009; *C. J. Somes and Oschlies*, 2015; *Srinivas and Sarin*, 2013]. Hence it is coupled to the larger ocean biogeochemical cycle, particularly N loss processes [*Landolfi et al.*, 2015; *Mahaffey et al.*, 2005; *Meyer et al.*, 2016; *J K Moore and Doney*, 2007; *J K Moore et al.*, 2006; *C. J. Somes et al.*, 2013]. Nitrogen fixation is also known to be suppressed by the presence of dissolved nitrogen

species in the water column. This physiological suppression effect is species dependent, but the available evidence [Grosskopf and LaRoche, 2012; Krupke et al., 2015; Meyer et al., 2016; Sohm et al., 2011] suggests that this only occurs at relatively high dissolved N concentrations (several μM). This threshold is much higher than the likely increase in surface water nitrogen concentrations from individual atmospheric N deposition events over the open ocean [Duce et al., 2008; Grosskopf and LaRoche, 2012; Michaels et al., 1993; Christopher J. Somes et al., 2016], which are likely to be in the range of nM rather than μM [Michaels et al., 1993]. This argument suggest suppression of nitrogen fixation by atmospheric deposition events is unlikely. However, this assertion merits further study both in field populations, mesocosms and in laboratory cultures, although this is challenging because only a few nitrogen fixing marine microbes are currently in culture. In our modelling of the N cycle here we evaluate the impacts of atmospheric deposition on the oceans with and without this potential inhibition of nitrogen fixation (see later).

We suggest that nitrogen fixation rates are unlikely to change in the near future as a result of anthropogenic N inputs to the ocean. However, changes in dust input might change the iron supply and hence change the rates [Ito et al., 2016; T. D. Jickells et al., 2005; J K Moore et al., 2006] as may ocean acidification [Hutchins et al., 2015].

Atmospheric deposition

The third important external source of fixed nitrogen to the oceans is from the atmosphere. As a result of anthropogenic nitrogen emissions, the total atmospheric nitrogen input to the ocean is now comparable in magnitude to the other external nitrogen sources, although the balance between them will vary regionally. The atmospheric input is made up of inorganic oxidized (nitrate and nitric acid) and reduced (ammonia and ammonium) nitrogen and organic nitrogen. In this context, organic nitrogen is defined as nitrogen available to inorganic nitrogen analysis after oxidation [Cape et al.,

2011]. On a global basis these three forms contribute in approximately equal amounts to the total nitrogen deposition [Duce *et al.*, 2008; Kanakidou *et al.*, 2012] although there are substantial temporal and regional variations in fluxes and composition as discussed later. Atmospheric nitrogen fluxes are now greatly enhanced (approximately 10 fold) by human activity. Combustion is the main source of oxidised nitrogen, emitted as NO_x and converted on timescales of a day or so to nitric acid and nitrate. Agricultural emissions are the main source of ammonia [Duce *et al.*, 2008]. Most emissions originate on land, although shipping emissions are becoming increasingly important [Eyring *et al.*, 2005 and Table 1]. Rapid and efficient atmospheric transport allows these emissions to reach the open oceans within days, hence much faster and more effectively than fluvial inputs [Fowler *et al.*, 2013].

The magnitude of nitrogen emissions and their deposition to the oceans are uncertain and generally poorly constrained by both data and models. However, a recent detailed comparison of models and data for the Atlantic Ocean suggested reasonable agreement between model estimates and observations, providing increased confidence in the estimates presented here [Baker *et al.*, 2010 and Baker *et al.*, in prep].

The estimates of atmospheric deposition here are based on the TM4-ECPL model [Daskalakis *et al.*, 2015; Tsigaridis *et al.*, 2014] which includes for the first time an explicit scheme for estimating atmospheric dissolved organic nitrogen deposition [Kanakidou *et al.*, 2012]. In contrast Duce *et al.* [2008] ran their present day simulation of atmospheric nitrogen deposition for the year 2000 based on a synthesis of global models [Dentener *et al.*, 2006]. The simulation reported here is for 2005, although the impacts of this change in year are trivial, when considering the large spatial scales here. The estimates from the TM4-ECPL model agree well with other model outputs and with data [Kanakidou *et al.*, 2016]. The spatial distribution derived from the TM4-ECPL model of nitrogen deposition (Figure 3) and present-day global nitrogen emission estimates (Table 1, 125 Tg N yr⁻¹) are very similar to those in Duce *et al.* [2008], 116 (uncertainty range 68-164)TgN yr⁻¹. However, the net

nitrogen deposition estimates to the oceans (Table 2) are rather different as discussed below, with a net deposition here of 39 Tg N yr⁻¹ compared to 67 (uncertainty range 38-96) Tg N yr⁻¹ in Duce et al, (2008).

The difference reflects a slightly lower (18 vs 23 TgNyr⁻¹) oxidised nitrogen deposition to the ocean. This arises in part because some of the oxidized nitrogen emission is assumed to react to form atmospheric organic nitrogen (about 10 TgNyr⁻¹ produced mainly over land), of which 2 Tg N yr⁻¹ is deposited to the ocean [Kanakidou et al., 2012]. Other formation pathways for inorganic nitrogen involving ammonia have been suggested [Altieri et al., 2012]. The major differences between the budget here and that of Duce et al. (2008) reflects changes in the model estimates of net organic nitrogen and reduced inorganic nitrogen (NH₄⁺/ NH₃) deposition. This highlights the potential importance of the role of recycled marine emissions in these fluxes in particular, since re-deposition of marine emissions will not create a net increase in marine productivity. The specific major changes to these flux estimates compared to Duce et al. [2008] are detailed below;

- The TM4-ECPL explicit modelling of organic nitrogen yields a total deposition flux of dissolved organic nitrogen to the ocean of 15 TgN yr⁻¹, somewhat lower than the flux of 20 (uncertainty range 10-30) TgN yr⁻¹ estimated by [Duce et al., 2008] who used a simple assumption (based on literature estimates) that DON represents 30% of total N deposition. The deposited DON has uncertain, complex and poorly quantified sources that may include some marine emissions that are re-deposited [T.D. Jickells et al., 2013]. TM4 model estimates about 6 TgNyr⁻¹ of this DON to be of marine origin and redeposited to the ocean, resulting in a net flux of 9 TgNyr⁻¹. This estimation of an important recycled marine component of DON is consistent with estimates from observational studies on Bermuda [Altieri et al., 2016], although at other locations anthropogenic terrestrial sources have been argued to dominate the DON [T.D. Jickells et al., 2013]. The DON model results reported here estimate gross DON deposition at 15-20% of total N deposition (Figure 4) which is

broadly in line with recent measurements of the proportion of DON in aerosols and rainwater over the Atlantic – 7-10% [Zamora *et al.*, 2011], ~24% [Lesworth *et al.*, 2010] and 19% [Altieri *et al.*, 2016] and Pacific - 16% [Martino *et al.*, 2014]. However, the proportion varies greatly regionally from 4-62% [Zamora *et al.*, 2011]. Thus the major change in the flux estimate here compared to that of Duce *et al.* (2008) is the suggestion that the gross DON deposition may include an important marine recycled component, leading to a reduction in the net DON deposition. The sources of organic nitrogen in marine deposition are uncertain and there is also evidence for an important terrestrial and anthropogenic component to the deposition [Cape *et al.*, 2011]. Hence further studies of atmospheric organic nitrogen are required.

- In the case of reduced nitrogen (NH_x = ammonia+ammonium), the new model estimate of ammonia/ammonium deposition to the oceans presented here (12 Tg N yr^{-1}) is only half of that reported by Duce *et al.* [2008], 24 (uncertainty range 14-32) TgN yr^{-1} . This difference arises because in the new model estimate, while gross NH_x deposition is 20 TgN yr^{-1} (broadly similar to the earlier estimate), 8 TgN yr^{-1} of this are estimated to be associated with re-deposition of NH_x emitted as ammonia from the oceans. This compares to an estimate of recycled ammonia of only 3 TgN yr^{-1} in Duce *et al.* [2008]. Thus, as with the dissolved organic nitrogen, the marine recycling flux estimation results in an important change in the net flux estimates. There is relatively limited direct experimental evidence to substantiate the large-scale marine emission of ammonia suggested by these models [Johnson *et al.*, 2008], but it is consistent with one recent detailed study on Bermuda in the tropical Atlantic [Altieri *et al.*, 2014]. We suggest that the magnitude and direction of the air-sea ammonia flux (and the organic nitrogen flux) deserves further investigation.

Table 1 TM4-ECPL Model estimated global atmospheric N emissions by source for 1850, 2005 and 2050, the latter based on the RCP6.0 scenario

<u>Emissions Tg N yr⁻¹</u>			
Source	1850	2005	2050
NOx			
Terrestrial Anthropogenic NOx	0.6	27	20.2
Shipping NOx		5.3	3.1
Aircraft NOx		0	0
Biomass Burning NOx	0.5	5.5	5.7
Natural NOx Soils+ lightening	11.8	11.6	11.6
NHx			
Terrestrial Anthropogenic NHx	5.4	32.9	43.7
Biomass burning NHx	0.9	9.2	9.4
Natural NHx soils	2.4	2.4	2.4
Natural NHx ocean emissions	8.2	8.2	8.2
Total inorganic N	29.8	102.1	104.3
Organic N (ON)			
Anthropogenic and biomass burning	1.3	7.0	6.8
Natural biogenic particles and soil dust	9.3	9.3	9.3
ON insoluble on marine aerosol	1.1	1.1	1.1
ON soluble on marine aerosol and marine amines	5.8	5.8	5.8
Total ON	17.5	23.2	23
Total N emissions	47.2	125.2	127.3

Table 2 Deposition to the Oceans Tg N yr⁻¹
all with 2005 meteorology and using the RCP 6.0 scenario for 2050

Flux	1850	2005	2050
Inorganic NOy	4	18	13
NHy from land	2	12	14
NHy from ocean (redeposited)	8	8	8
ON from land	4	9	9
ON from ocean recycled	6	6	6
Total N input	24	53	50
Net N input	10	39	36

Note total N includes insoluble organic nitrogen

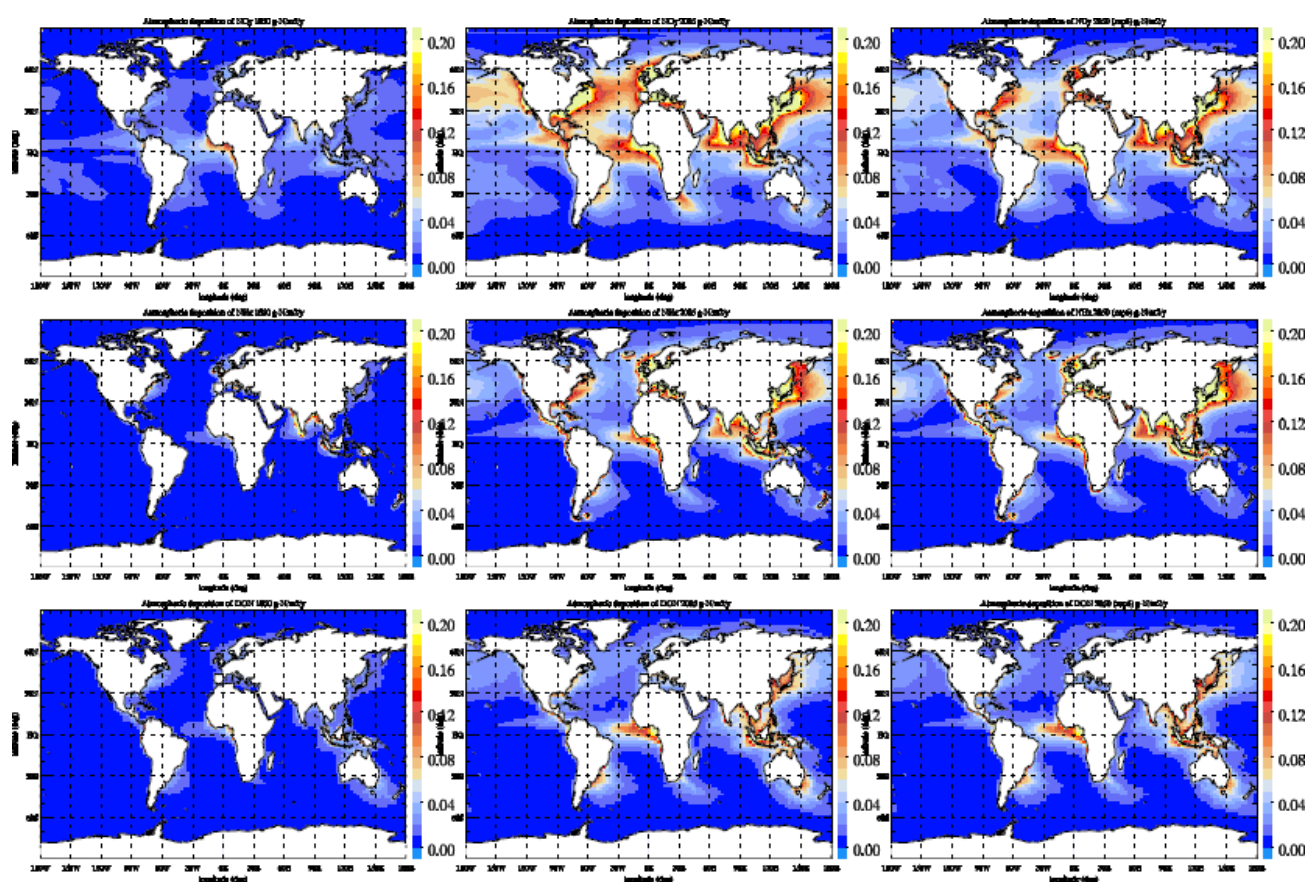


Figure 3 Deposition fields to the oceans for 1850 (left column), 2005 (middle column) and 2050 (right column) for Oxidised (NO_y) upper panels, Reduced (NH_x) middle panels and Organic N lower panels (in g N m⁻² yr⁻¹, scale maximum has been fixed to 0.20 for readability and easier comparison).

Despite the changes in the overall fluxes, the geographic patterns of atmospheric deposition to the oceans and their temporal evolution (Figure 3) remain similar to those of Duce et al., [2008]. Highest inputs occur in the northern hemisphere downwind of large industrial and population centres in Europe, North America and Asia. The model does not have sufficient resolution to separate deposition to coastal waters from that to the open ocean accurately, but Vet et al. [2014] suggest that 24% of nitrogen deposition falls in the coastal region as they define it. Because Vet et al. [2014]

use a definition which includes some coastal land area, 24% probably represents an upper limit on the total of atmospheric nitrogen deposition that falls onto the coastal seas.

Atmospheric N inputs to the oceans are estimated to have increased sharply from 1860 to 2005 particularly in areas such as the North Atlantic and North Pacific downwind of industrialised regions. The increases in deposition to the South China Sea, for example, are already evident and now appear to be directly impacting local water-column nitrate concentrations and primary production [*I N Kim et al.*, 2014; *T W Kim et al.*, 2014]. It has recently been argued that atmospheric deposition of nutrients (particularly iron, but also nitrogen) to the western Pacific can have impacts further afield in the eastern tropical Pacific, following transportation of atmospherically deposited nutrients by the ocean circulation [*Ito et al.*, 2016].

Most emission scenarios to 2050 suggest further atmospheric deposition increases will be seen predominantly downwind of southern and south-east Asia, reflecting industrial development plus population and affluence increases. Current projections for 2030 and 2100 under different RCP scenarios [*Kanakidou et al.*, 2016] suggest total N deposition to the oceans will change little between now and 2100 (-2 to +7% change by 2030, -17 to +8% by 2100 which is somewhat smaller than the projection with a different scenario of Duce et al. [2008]). However, the global distribution pattern will probably change [Figure 3 and *Duce et al.*, 2008]. The balance of the relative importance of oxidized (derived from NO_x emissions) and reduced nitrogen (derived from ammonia emissions) is also projected to change, with an increasing proportion of ammonium compared to nitrate, due to more efficient controls on terrestrial NO_x emissions compared to ammonia [*Lamarque et al.*, 2013]. These trends are already evident in deposition data with reduced nitrogen becoming relatively more important in North America in recent years [*Vet et al.*, 2014]. The trend in Southeast Asia is the reverse [*Liu et al.*, 2013] in each case reflecting regional emission changes. There are also currently large regional differences in the relative importance of oxidized and reduced nitrogen in atmospheric deposition, with the proportion of reduced to total nitrogen in deposition much higher

in S E Asia than elsewhere [Vet *et al.*, 2014]. The suggested trend to a greater relative proportion of reduced to oxidised nitrogen can potentially alter atmospheric aerosol pH and the acidity of atmospheric deposition [Lamarque *et al.*, 2013]. However, this may not necessarily be the case, at least over land, where aerosol gas phase interactions maintain very acidic aerosol pH values until the ratio of acids to ammonia gas falls quite low [R J Weber *et al.*, 2016].

Summary of Estimated Inputs

In Table 3 we present a summary of our best estimates of contemporary nitrogen inputs to the oceans, based on the earlier discussion in the text. We therefore suggest that at least 76% of the atmospheric input is deposited beyond the shelf break, and 75% of the river DIN input escapes beyond the shelf break. We assume all of the nitrogen fixation takes place in the open ocean. Based on the scenarios discussed earlier, it seems likely that total fluxes of nitrogen to the ocean are unlikely to change markedly over the next few decades, assuming the scenarios considered are realistic.

Table 3 Nitrogen Inputs to the total oceans including the continental shelf, and to the open ocean beyond the shelf break, see text for derivation of numbers.

Source	Total ocean Flux Tg N y ⁻¹	Flux to the open ocean Tg N y ⁻¹
Atmospheric	39	>30
Fluvial	DIN 23, DON 11	DIN 17, Don >0 to <11
N fixation	164	164

Impacts of atmospheric deposition on water column productivity

The effects of atmospheric deposition have been evaluated previously using global ocean biogeochemical models [Krishnamurthy *et al.*, 2007; Krishnamurthy *et al.*, 2010; Krishnamurthy *et al.*, 2009; Suntharalingam *et al.*, 2012; Yang and Gruber, 2016] or based on various scaling procedures by Duce *et al.* [2008]. Duce *et al.* (2008) and Suntharalingam *et al.* (2012) use the same atmospheric deposition field, while Krishnamurthy *et al.* (2012) use a separately derived field with a somewhat smaller flux, due in part to not considering organic nitrogen, and also using net rather

than gross ammonia/ammonium inputs, i.e. correcting for the marine ammonia emissions. All three of these models estimate the impact of increased atmospheric N-deposition on export production (that which sinks to depth and should relate to ocean biological CO₂ uptake) to be ~ 0.4PgC/yr, reflecting predominantly the similar atmospheric nitrogen inputs used in each of the different model simulation. Studies have also considered the impact of atmospheric deposition at regional scales [*Ito et al.*, 2016; *Sundarambal et al.*, 2010; *Zamora et al.*, 2010], finding for example that atmospheric deposition can sustain 3% of new primary production in the Northern Indian Ocean, and on occasions an even higher percentage in the Atlantic [*Singh et al.*, 2012; *Spokes et al.*, 2000].

The response of the oceans to the atmospheric inputs of nitrogen has been modelled here using the PlankTOM10 model [*Le Quere et al.*, 2005; *Le Quere et al.*, 2016] to which we have added the N₂O model of *Suntharalingam et al.* [2012]. This global biogeochemical model has a 2*1.1 degree resolution, 10 plankton functional types and 44 state variables run within an ocean general circulation model. The model allows variable Fe:Chl:Si:C ratios in phytoplankton and POM [*Buitenhuis et al.*, 2013], fixed O₂:C:N:P in all organic matter [*Anderson and Sarmiento*, 1994] and allows nitrogen fixing organisms to preferentially utilize dissolved nitrogen in the water column when it is available. The atmospheric deposition field is essentially the same as that described earlier from the TM4 model, although the total flux used in the runs here was 35 rather than 39 Tg N yr⁻¹ with deposition fields as in Figure 3. The PlankTOM10 nitrogen fixation field is shown in Figure 2 and discussed earlier. The PlankTOM10 model does not fully resolve the shelf sea because of the grid square resolution, so we have used a value of riverine N input to the ocean of 16.3TgN/yr, similar to the estimated total DIN net river input to the open ocean. *Da Cuna et al* [2007], have previously shown, using an earlier version of this model, that the ocean productivity is relatively insensitive (on decadal time scales) to changes in the river input; for example primary and export productivity only decrease by 7% and 3% respectively for a complete cessation of river inputs in the model runs, while only a 5% increase in primary productivity results from a 50% increase in riverine N inputs. However, the percentage impact on the coastal ocean productivity in each case is greater.

In the standard PlankTOM10 configuration, nitrogen fixation suppression increases with increasing surface water nitrogen concentrations, and is suppressed by 50% at $1.7 \mu\text{M NH}_4$ or $7.3 \mu\text{M NO}_3$. This is based on the assumption that nitrogen fixing organisms would preferentially utilise available fixed nitrogen in the water column. This creates a potential negative feedback on ocean nitrogen cycle from atmospheric deposition as less nitrogen is fixed if there is an increase in nitrogen deposition. As noted above, some of the available evidence suggests that such suppression only occurs at high surface water fixed N concentrations, and that therefore individual atmospheric deposition events are unlikely to lead to such large increases in ambient surface water nitrogen concentrations. We have performed two model simulations, one assuming no suppression of nitrogen fixation by fixed nitrogen (Table 4A) and the other retaining the standard PlankTOM10 suppression (Table 4B). The model runs covered just over 400 years. Overall, ocean nitrogen fixation without the suppression is increased by 18 (from 146 to 164) Tg N yr^{-1} (12% increase) over the standard run with suppression, emphasising the potential sensitivity of the ocean biogeochemical system to such suppression as a negative feedback. Note also that nitrogen fixation is still reduced by about 4% in the model runs without suppression compared to the pre-industrial run. This may reflect non-nitrogen fixing phytoplankton outcompeting nitrogen fixers for other key nutrients (Fe and P), and thereby suppressing the growth of nitrogen fixers. Others have reported a similar reductions in nitrogen fixation due to atmospheric nitrogen deposition in their model runs [*Krishnamurthy et al.*, 2007; *Krishnamurthy et al.*, 2010; *Krishnamurthy et al.*, 2009; *Okin et al.*, 2011; *Christopher J. Somes et al.*, 2016].

Somes et al [2016] have recently reported a related study of the impacts of atmospheric deposition on ocean productivity using the UVic Earth System Climate Model. This model has more complex feedbacks than the PlankTOM10 model, particularly in terms of benthic and pelagic denitrification, However, this model does not resolve shelf systems well, and so underestimates benthic denitrification and thereby also nitrogen fixation, which is set in the model to balance the overall denitrification losses. The Somes et al. [2016] simulations estimated the impact of atmospheric

nitrogen inputs to the ocean at the upper end of the flux ranges considered by Duce et al. [2008].

The UVic model is parameterised such that at 5µM nitrate, nitrogen fixation is fully suppressed. The UVic model, like the PlankTOM10 model, therefore also produces quite a strong negative feedback from the suppression of nitrogen fixation by atmospheric nitrogen deposition. This model also highlights another potentially important feedback [Landolfi et al., 2013]. Denitrification consumes more nitrogen than is liberated from its decomposition of organic matter. Hence it has been demonstrated in the UVic model that increased atmospheric nitrogen deposition can lead to a negative feedback, in which increased production leads to expansion of low oxygen zones, and then to net nitrogen consumption by denitrification, and hence to lower overall ocean productivity. This feedback occurs on times scales of hundreds of years reflecting the ocean circulation timescales for passing water through denitrification zones [Christopher J. Somes et al., 2016]. Yang and Gruber (2016) reached a very similar conclusion using a different ocean biogeochemical model.

The model estimates here consider mainly the effects of nitrogen deposition on nitrogen fixation. However, there is increasing evidence that atmospheric iron deposition also plays a key role in nitrogen fixation because of the high iron requirements of nitrogen fixing enzymes [Ito et al., 2016; Martino et al., 2014; C M Moore et al., 2009; Ward et al., 2013]. The dominance of nitrogen fixation we identify here, and the uncertainty in its sensitivity to atmospheric nitrogen and iron inputs and water column phosphorus cycling [Landolfi et al., 2015], suggests that the magnitudes and controls on nitrogen fixation merit further research.

In the subsequent discussion to illustrate the maximum potential effects, we consider the model output run without the suppression of nitrogen fixation (Table 4A rather than 4B). We derive the changes in various ocean biogeochemical processes compared to a pre-industrial atmospheric input estimate with the present day riverine nutrient input. As noted earlier, reducing the riverine input to preindustrial levels would have little impact on the outcome in most open ocean regions [da Cunha et al., 2007].

Our estimates (Table 3) indicate that atmospheric inputs dominate the increased N inputs to the oceans since the pre-industrial era. This is the case even allowing for the increased inputs from rivers to the open ocean estimated here, compared to the assumption by Duce et al. of complete shelf nitrogen retention (Table 3). There are strong spatial gradients in the atmospheric N deposition as discussed by Duce et al. (see also Figure 3) with much larger inputs to the northern hemisphere ocean compared to the southern hemisphere. Within the northern hemisphere, deposition is particularly high in ocean regions downwind of large population centres, such as Asia (Figure 3).

The model results (Table 4) suggest that increased anthropogenic atmospheric N deposition from preindustrial to the present could have increased ocean productivity overall by about 0.4% equivalent to 0.15PgC/yr. This increase in overall primary production is about half of that suggested by Duce et al. [2008] who's estimates were based on scaling atmospheric deposition falling on nitrogen limited ocean regions to primary production using the Redfield ratio. The difference between the estimates here (Table 4) and this earlier estimate is essentially consistent with the reduced net atmospheric nitrogen deposition estimated here compared to the earlier paper.

Export production is the proportion of the primary production sinking to the deep ocean and the key issue in terms of removal of CO₂ from the atmosphere [*Giering et al.*, 2014; *Laws et al.*, 2000]. Export production only increases by 0.01PgC/yr over the short term in the model runs (Table 4). The proportion of the primary production exported to depth estimated here is smaller than that estimated by Duce et al. [2008]. This low export percentage (f ratio - new or export/total primary production) estimate of only 7% in PlankTOM10 compared to an assumed value of 22% in Duce et al., is consistent with some other lower published estimates [e.g. *Laws et al.*, 2000]. Krishnamurthy et al [2007] have a similarly low sinking POC flux that is only 12% of productivity in their estimates of the impacts of atmospheric nitrogen deposition. Recently Henson et al. [2011] have also argued more generally for such a lower value for the f ratio, based on direct measurements, while also emphasising that the f ratio varies systematically throughout the oceans. Regardless of the short

term (years to decades) recycling of the atmospherically deposited nitrogen within the upper ocean and low export production, on the longer times scale (centuries) the atmospheric nitrogen input will eventually be lost to the deep sea and with it the associated draw down of 0.15 Pg C/yr , the model runs are simply not long enough to capture this effect.

N₂O, a powerful greenhouse gas released by nitrification and denitrification processes. Duce et al. [2008] noted that increases in ocean productivity can lead to expansion of low oxygen regions and an attendant increase in N₂O emissions. The extent of such a feedback is sensitive to the export production and also to the area and extent of low oxygen [e.g. *Bianchi et al.*, 2012]. The impacts of atmospheric nitrogen deposition on N₂O emissions by nitrification and denitrification have been modeled by Suntharalingam [2012]. In our model runs (Table 4) we estimate the low oxygen region for N₂O emissions, based on three different oxygen concentration thresholds of <20, 10 and 5μM oxygen concentration. In the model runs the areas of low oxygen, defined by all three thresholds, increase as does the overall ocean N₂O flux, but the increases are generally <1% (Table 4). This increase is smaller than the 3-4% change in N₂O emissions estimated by Suntharalingam et al. [2012]. This reduction is consistent with the reduced magnitude of net atmospheric anthropogenic nitrogen inputs used here compared to those used by Suntharalingam et al. (2012). N₂O can also be produced by oxidation of ammonia and DON, and changes in the surface ocean cycling of these species as a result of atmospheric deposition could also change the ocean emissions of N₂O [*Loscher et al.*, 2012; *Santoro et al.*, 2011]. Although there are substantial uncertainties associated with all aspects of the oceanic N₂O cycle [*Zamora and Oschlies*, 2014], the small size of change in N₂O emissions estimated here suggests that large changes in N₂O because of atmospheric nitrogen deposition are unlikely.

Conclusions

The combination of lower atmospheric deposition fluxes estimated here compared to earlier studies, a relatively high estimated rate of nitrogen fixation, and ocean biogeochemical feedbacks leads to a prediction of a smaller impact of increasing atmospheric nitrogen deposition on ocean

biogeochemical cycles and carbon uptake than that of Duce et al. [2008]. Our estimate of the flux of fluvial nitrogen to the open ocean is larger. The analysis and model calculations presented here highlight that this conclusion is very sensitive to four feedbacks which we identify – recycling of ammonia and organic nitrogen from seawater to the atmosphere, inhibition of nitrogen fixation by atmospheric nitrogen deposition and the denitrification sink for nitrogen. All these feedbacks undoubtedly occur, so the key, and very difficult, challenge is the quantification of the scale of these under realistic open ocean conditions.

The calculations here suggest that the impacts of atmospheric deposition on ocean biogeochemistry can result in a net increase in primary production and CO₂ uptake of 0.15 Pg C yr⁻¹. However, the resulting reduction in radiative forcing will be offset slightly by increases in N₂O emissions from some regions of the oceans [Suntharalingam et al., 2012].

In some areas pulses of atmospheric nutrient deposition may be sufficiently large to have short term (days) impacts on productivity [Guieu et al., 2014]. However, over most of the oceans the likely scale of short-term nitrogen inputs are relatively small compared to the existing background stock [Duce et al., 2008; Michaels et al., 1993]. This may not be the case for dust/iron deposition which can affect nitrogen fixation [Guieu et al., 2014; J K Moore et al., 2006].

The increases in fluvial nitrogen inputs to the ocean from human activity predominantly affect coastal systems leading to major environmental pressures [e.g. Diaz and Rosenberg, 2008]. We suggest a quarter of fluvial inorganic nitrogen inputs are denitrified on the shelf, and the fate of fluvial dissolved organic nitrogen is particularly uncertain. Our results suggest that the effects of shelf denitrification on fluvial dissolved inorganic nitrogen fluxes is strongly latitude dependent, and further increases in nitrogen use on land in equatorial regions may therefore have a disproportionately large impact on total fluvial inputs to the open ocean. Where there are large losses of fluvial inorganic nitrogen by denitrification on the shelf, this may result in excess fluvial P inputs to the open ocean (relative to N) which could then support nitrogen fixation.

In general the impacts of atmospheric nitrogen deposition will be greatest where the ambient surface water column nitrogen concentrations are low and hence in the ocean gyres [Duce *et al.*, 2008]. Atmospheric nitrogen deposition has strong geographic gradients, and thus it is important to consider regions where the impacts of atmospheric deposition may be particularly strong, or rather different to the general pattern. We identify four such regions – the North Pacific, North Indian Ocean, Mediterranean and tropical North Atlantic as explained below.

We predict (Figure 3) as previously [Duce *et al.*, 2008] that the western North Pacific is likely to be a focus of increasing atmospheric deposition over coming decades, even if the total net nitrogen input to the oceans may not grow. Deposition in this region is already argued to be increasing ocean productivity regionally [I N Kim *et al.*, 2014; T W Kim *et al.*, 2014]. This regional impact may be extended beyond the regions of enhanced atmospheric deposition via ocean circulation transport of deposited nutrients, where this can occur relatively rapidly on timescales of decades or less [Ito *et al.*, 2016].

In the northern Indian Ocean region, atmospheric deposition is already estimated to be contributing to new production [Singh *et al.*, 2012] and is predicted to increase. This region also contains a major deep water oxygen minimum zone where denitrification and nitrification sustain very high N₂O fluxes. Here increasing nutrient inputs may lead to intensification of hypoxic conditions and increased fluxes of the greenhouse gas N₂O, making this area of particular interest [Naqvi *et al.*, 2010; Suntharalingam *et al.*, 2012]. The Bay of Bengal region has low sub-surface oxygen concentrations, but minimal water column denitrification and N₂O production at present [Bristow *et al.*, 2017]. Even modest increases in export production in the future could lead to substantial denitrification and N₂O production.

The last areas we would highlight are the Mediterranean and North Atlantic subtropical gyre, which are both characterized by evidence of phosphorus limitation of primary production. This situation is enhanced by nitrogen deposition and may lead to accumulation of nitrogen in the water column and

different biogeochemical impacts in such regions [*Krom et al.*, 2010; *C M Moore et al.*, 2009; *Ward et al.*, 2013; *Yang and Gruber*, 2016; *Zamora et al.*, 2010], compared to other ocean regions where nitrogen may be the proximate limiting nutrient [*C M Moore et al.*, 2013].

Acknowledgements

This paper resulted from the deliberations of United Nations GESAMP Working Group 38, “The Atmospheric Input of Chemicals to the Ocean”. We thank the ICSU Scientific Committee on Oceanic Research, the U.S. National Science Foundation, the Global Atmosphere Watch and the World Weather Research Programme of the World Meteorological Organization, the International Maritime Organization, and the University of East Anglia for their support. All data used are available from the relevant references apart from the new Planktom model output which is publically available at <http://opendap.uea.ac.uk:8080/opendap/greenocean/PlankTOM10.2/contents.html> . The full Planktom manual is available on request from E. Buitenhuis.

We wish to gratefully acknowledge the very constructive and helpful reviews of an earlier version of this paper by Maren Voss and a second anonymous reviewer and also the support of the GBC editor Sara Mikaloff Fletcher. Their efforts have significantly improved this paper.

Table 1 TM4-ECPL Model estimated global atmospheric N emissions by source for 1850, 2005 and 2050, the latter based on the RCP6.0 scenario

<u>Emissions Tg N yr⁻¹</u>			
Source	1850	2005	2050
NOx			
Terrestrial Anthropogenic NOx	0.6	27	20.2
Shipping NOx		5.3	3.1
Aircraft NOx		0	0
Biomass Burning NOx	0.5	5.5	5.7
Natural NOx Soils+ lightening	11.8	11.6	11.6
NHx			
Terrestrial Anthropogenic NHx	5.4	32.9	43.7
Biomass burning NHx	0.9	9.2	9.4
Natural NHx soils	2.4	2.4	2.4
Natural NHx ocean emissions	8.2	8.2	8.2
Total inorganic N	29.8	102.1	104.3
Organic N (ON)			
Anthropogenic and biomass burning	1.3	7.0	6.8
Natural biogenic particles and soil dust	9.3	9.3	9.3
ON insoluble on marine aerosol	1.1	1.1	1.1
ON soluble on marine aerosol and marine amines	5.8	5.8	5.8
Total ON	17.5	23.2	23
Total N emissions	47.2	125.2	127.3

Table 2 Deposition to the Oceans Tg N yr⁻¹
all with 2005 meteorology and using the RCP 6.0 scenario for 2050

Flux	1850	2005	2050
Inorganic NOy	4	18	13
NHy from land	2	12	14
NHy from ocean (redeposited)	8	8	8
ON from land	4	9	9
ON from ocean recycled	6	6	6
Total N input	24	53	50
Net N input	10	39	36

Note total N includes insoluble organic nitrogen

Table 3 Nitrogen Inputs to the total oceans including the continental shelf, and to the open ocean beyond the shelf break, see text for derivation of numbers.

Source	Total ocean Flux Tg N γ^{-1}	Flux to the open ocean Tg N γ^{-1}
Atmospheric	39	>30
Fluvial	DIN 23, DON 11	DIN 17, Don >0 to <11
N fixation	164	164

Table 4. Mean global-scale fluxes averaged over the 1990s are given for PlankTOM10- (2*1.1 degree resolution) [Buitenhuis *et al.*, 2013; Le Quere *et al.*, 2005]. Values in parentheses show the percent difference in each flux when rising atmospheric N deposition is included. Nitrogen fluxes are given in units of TgN/yr and carbon fluxes are in units of PgC/yr. Total changes (Δ) in the atmospheric nitrogen inputs and their impacts on nitrogen fixation, denitrification, primary production and N₂O emissions are also listed.

A Model run without nitrogen fixation suppression

	PlankTOM10	Δ TgN/yr
Atm N Deposition a	35(177)	22.3
Riverine N Inputs b	16.3(0)	
Nitrogen Fixation	164(-3.9)	-6.74
Denitrification c	212(1.7)	3.53
Sed Norg Burial	57.7g(0)	
Primary Production	33.6(0.44) 5135TgN	22.49
Sinking POC Export@100m d	2.96(0.35) 453 2.14	
Air-Sea CO ₂ Flux	2.83(0.00)	
Air-Sea N ₂ O Flux	2.07(0.5)	0.01
OMZ Volume- 20 μ M e	16.9e15m ³ (0.86)	
OMZ Volume- 10 μ M	3.58 e15m ³ (0.38)	
OMZ Volume- 5 μ M	1.19 e15m ³ (3.7)	

B Model run including N fixation suppression

	PlankTOM10	Δ TgN/yr
Atm N Deposition a	35(179)	22.5
Riverine N Inputs b	16.3(0)	
Nitrogen Fixation	146(-7.0)	-11.33
Denitrification c	207(1.8)	3.65
Sed Norg Burial	57.7g(0)	
Primary Production	33.7(0.42) 5158TgN	20.94
Sinking POC Export@100m d	2.99(0.54) 457.4 2.37	
Air-Sea CO ₂ Flux	2.88(0.17)	
Air-Sea N ₂ O Flux	2.55(0.8)	0.02
OMZ Volume- 20 μ M e	16.35e15m ³ (0.43)	
OMZ Volume- 10 μ M	3.38 e15m ³ (1.8)	
OMZ Volume- 5 μ M	1.13 e15m ³ (1.5)	

a&b – dissolved inorganic N + dissolved organic N

c – all as water column denitrification in model

d – sinking particulate organic carbon at 100m

e – volume of oxygen minimum zone waters at specified cutoff value

References

- Altabet, M. A., M. J. Higginson, and D. W. Murray (2002), The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO₂, *Nature*, *415*(6868), 159-162, doi: 10.1038/415159a.
- Altieri, K. E., M. G. Hastings, A. J. Peters, and D. M. Sigman (2012), Molecular characterization of water soluble organic nitrogen in marine rainwater by ultra-high resolution electrospray ionization mass spectrometry, *Atmos Chem Phys*, *12*(7), 3557-3571, doi: 10.5194/acp-12-3557-201.
- Altieri, K. E., M. G. Hastings, A. J. Peters, S. Oleynik, and D. M. Sigman (2014), Isotopic evidence for a marine ammonium source in rainwater at Bermuda, *Global Biogeochem Cy*, *28*(10), 2014GB004809, doi: 10.1002/2014GB004809.
- Altieri, K. E., S. E. Fawcett, A. J. Peters, D. M. Sigman, and M. G. Hastings (2016), Marine biogenic source of atmospheric organic nitrogen in the subtropical North Atlantic, *P Natl Acad Sci USA*, *113*(4), 925-930, doi: 10.1073/pnas.1516847113.
- Anderson, L. A., and J. L. Sarmiento (1994), Redfield Ratios of Remineralization Determined by Nutrient Data-Analysis, *Global Biogeochem Cy*, *8*(1), 65-80
- Baker, A. R., T. Lesworth, C. Adams, T. D. Jickells, and L. Ganzeveld (2010), Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50 degrees N to 50 degrees S based on large-scale field sampling: Fixed nitrogen and dry deposition of phosphorus, *Global Biogeochem Cy*, *24*, GB3006, doi: Doi 10.1029/2009gb003634.
- Benavides, M., D. A. Bronk, N. S. R. Agawin, M. D. Perez-Hernandez, A. Hernandez-Guerra, and J. Aristegui (2013), Longitudinal variability of size-fractionated N₂ fixation and DON release rates along 24.5 degrees N in the subtropical North Atlantic, *J Geophys Res-Oceans*, *118*(7), 3406-3415
- Beusen, A. H. W., A. F. Bouwman, L. P. H. Van Beek, J. M. Mogollón, and J. J. Middelburg (2016), Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum, *Biogeosciences*, *13*(8), 2441-2451, doi: 10.5194/bg-13-2441-2016.
- Bianchi, D., J. P. Dunne, J. L. Sarmiento, and E. D. Galbraith (2012), Data-based estimates of suboxia, denitrification, and N₂O production in the ocean and their sensitivities to dissolved O₂, *Global Biogeochem Cy*, *26*(2), n/a-n/a, doi: 10.1029/2011GB004209.
- Bombar, D., R. W. Paerl, and L. Riemann (2016), Marine Non-Cyanobacterial Diazotrophs: Moving beyond Molecular Detection, *Trends Microbiol.*, *24*(11), 916-927, doi: 10.1016/j.tim.2016.07.002.
- Bristow, L. A., et al. (2017), N₂ production rates limited by nitrite availability in the Bay of Bengal oxygen minimum zone, *Nature Geosci*, *10*(1), 24-29, doi: 10.1038/ngeo2847.
- Buitenhuis, E. T., T. Hashioka, and C. Le Quere (2013), Combined constraints on global ocean primary production using observations and models, *Global Biogeochem Cy*, *27*(3), 847-858, doi: Doi 10.1002/Gbc.20074.
- Cape, J. N., S. E. Cornell, T. D. Jickells, and E. Nemitz (2011), Organic nitrogen in the atmosphere - Where does it come from? A review of sources and methods, *Atmos Res*, *102*(1-2), 30-48, doi: DOI 10.1016/j.atmosres.2011.07.009.
- Codispoti, L. A. (2007), An oceanic fixed nitrogen sink exceeding 400 Tg N a⁻¹ vs the concept of homeostasis in the fixed-nitrogen inventory, *Biogeosciences*, *4*(2), 233-253, doi: doi:10.5194/bg-4-233-2007.
- da Cunha, L. C., E. T. Buitenhuis, C. Le Quere, X. Giraud, and W. Ludwig (2007), Potential impact of changes in river nutrient supply on global ocean biogeochemistry, *Global Biogeochem Cy*, *21*(4), doi: Doi 10.1029/2006gb002718.
- Dabundo, R., M. F. Lehmann, L. Treibergs, C. R. Tobias, M. A. Altabet, P. H. Moisander, and J. Granger (2014), The Contamination of Commercial N-15(2) Gas Stocks with N-15-Labeled Nitrate and Ammonium and Consequences for Nitrogen Fixation Measurements, *Plos One*, *9*(10), doi: 10.1371/journal.pone.0110335.
- Daskalakis, N., S. Myriokefalitakis, and M. Kanakidou (2015), Sensitivity of tropospheric loads and lifetimes of short lived pollutants to fire emissions, *Atmos Chem Phys*, *15*(6), 3543-3563

Dentener, F., et al. (2006), Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation, *Global Biogeochem Cy*, 20, GB4003, doi:4010.1029/2005GB002672

Diaz, R. J., and R. Rosenberg (2008), Spreading dead zones and consequences for marine ecosystems, *Science*, 321(5891), 926-929, doi: DOI 10.1126/science.1156401.

Duce, R. A., et al. (2008), Impacts of atmospheric anthropogenic nitrogen on the open ocean, *Science*, 320(5878), 893-897, doi: DOI 10.1126/science.1150369.

Dutkiewicz, S., B. A. Ward, F. Monteiro, and M. J. Follows (2012), Interconnection of nitrogen fixers and iron in the Pacific Ocean: Theory and numerical simulations, *Global Biogeochem Cy*, 26, doi: Doi 10.1029/2011gb004039.

Eyring, V., H. W. Kohler, J. van Aardenne, and A. Lauer (2005), Emissions from international shipping: 1. The last 50 years, *J Geophys Res-Atmos*, 110(D17), doi: 10.1029/2004JD005619.

Falkowski, P., R. T. Barber, and V. Smetacek (1998), Biogeochemical controls and feedbacks on ocean primary production, *Science*, 281(5374), 200-206

Falkowski, P., et al. (2000), The global carbon cycle: A test of our knowledge of earth as a system, *Science*, 290(5490), 291-296

Fennel, K., J. Wilkin, J. Levin, J. Moisan, J. O'Reilly, and D. Haidvogel (2006), Nitrogen cycling in the Middle Atlantic Bight: Results from a three-dimensional model and implications for the North Atlantic nitrogen budget, *Global Biogeochem Cy*, 20(3), doi: 10.1029/2005GB002456.

Fowler, D., et al. (2013), The global nitrogen cycle in the twenty-first century, *Philos T R Soc B*, 368(1621), doi: Doi 10.1098/Rstb.2013.0164.

Gandhi, N., A. Singh, S. Prakash, R. Ramesh, M. Raman, M. S. Sheshshayee, and S. Shetye (2011), First direct measurements of N₂ fixation during a Trichodesmium bloom in the eastern Arabian Sea, *Global Biogeochem Cy*, 25, doi: 10.1029/2010GB003970.

Giering, S. L. C., et al. (2014), Reconciliation of the carbon budget in the ocean's twilight zone, *Nature*, 507(7493), 480-+

Grosskopf, T., and J. LaRoche (2012), Direct and indirect costs of dinitrogen fixation in *Crocospira watsonii* WH8501 and possible implications for the nitrogen cycle, *Front. Microbiol.*, 3, doi: 10.3389/fmicb.2010.00236.

Grosskopf, T., W. Mohr, T. Baustian, H. Schunck, D. Gill, M. M. M. Kuypers, G. Lavik, R. A. Schmitz, D. W. R. Wallace, and J. LaRoche (2012), Doubling of marine dinitrogen-fixation rates based on direct measurements, *Nature*, 488(7411), 361-364, doi: 10.1038/nature11338.

Gruber, N., and J. N. Galloway (2008), An Earth-system perspective of the global nitrogen cycle, *Nature*, 451(7176), 293-296, doi: 10.1038/nature06592.

Guieu, C., C. Ridame, E. Pulido-Villena, M. Bressac, K. Desboeufs, and F. Dulac (2014), Impact of dust deposition on carbon budget: a tentative assessment from a mesocosm approach, *Biogeosciences*, 11(19), 5621-5635, doi: 10.5194/bg-11-5621-2014.

Hansell, D. A. (2013), Recalcitrant Dissolved Organic Carbon Fractions, *Annu Rev Mar Sci*, 5, 421-445, doi: 10.1146/annurev-marine-120710-100757.

Henson, S. A., R. Sanders, E. Madsen, P. J. Morris, F. Le Moigne, and G. D. Quartly (2011), A reduced estimate of the strength of the ocean's biological carbon pump, *Geophys Res Lett*, 38

Hutchins, D. A., N. G. Walworth, E. A. Webb, M. A. Saito, D. Moran, M. R. McIlvin, J. Gale, and F. X. Fu (2015), Irreversibly increased nitrogen fixation in *Trichodesmium* experimentally adapted to elevated carbon dioxide, *Nat Commun*, 6

Ito, T., A. Nenes, M. S. Johnson, N. Meskhidze, and C. Deutsch (2016), Acceleration of oxygen decline in the tropical Pacific over the past decades by aerosol pollutants, *Nature Geosci*, 9(6), 443-447, doi: 10.1038/ngeo2717.

Jickells, T. D., and K. Weston (2011), 5.08 - Nitrogen Cycle – External Cycling: Losses and Gains, in *Treatise on Estuarine and Coastal Science*, edited, pp. 261-278, Academic Press, Waltham.

Jickells, T. D., A. R. Baker, J. N. Cape, S. E. Cornell, and E. Nemitz (2013), The cycling of organic nitrogen through the atmosphere, *Philos T Roy Soc B*, 368, 20130115, doi: 10.1098/rstb.2013.0115.

Jickells, T. D., et al. (2005), Global iron connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308(5718), 67-71, doi: DOI 10.1126/science.1105959.

Johnson, M. T., P. S. Liss, T. G. Bell, T. J. Lesworth, A. R. Baker, A. J. Hind, T. D. Jickells, K. F. Biswas, E. M. S. Woodward, and S. W. Gibb (2008), Field observations of the ocean-atmosphere exchange of ammonia: Fundamental importance of temperature as revealed by a comparison of high and low latitudes, *Global Biogeochem Cy*, 22(1), doi: Doi 10.1029/2007gb003039.

Kanakidou, M., S. Myriokefalitakis, N. Daskalakis, G. Fanourgakis, A. Nenes, A. R. Baker, K. Tsigaridis, and N. Mihalopoulos (2016), Past, Present, and Future Atmospheric Nitrogen Deposition, *Journal of the Atmospheric Sciences*, 73(5), 2039-2047, doi: doi:10.1175/JAS-D-15-0278.1.

Kanakidou, M., et al. (2012), Atmospheric fluxes of organic N and P to the global ocean, *Global Biogeochem Cy*, 26, GB3026, doi:3010.1029/2011GB004277, doi: 10.1029/2011GB004277.

Kim, I. N., K. Lee, N. Gruber, D. M. Karl, J. L. Bullister, S. Yang, and T. W. Kim (2014), Increasing anthropogenic nitrogen in the North Pacific Ocean, *Science*, 346(6213), 1102-1106

Kim, T. W., K. Lee, R. Duce, and P. Liss (2014), Impact of atmospheric nitrogen deposition on phytoplankton productivity in the South China Sea, *Geophysical Research Letters*, 41(9), 3156-3162, doi: Doi 10.1002/2014gl059665.

Krishnamurthy, A., J. K. Moore, C. S. Zender, and C. Luo (2007), Effects of atmospheric inorganic nitrogen deposition on ocean biogeochemistry, *J Geophys Res-Bioge*, 112(G2), G02019, doi:02010.01029/02006JG000334

Krishnamurthy, A., J. K. Moore, N. Mahowald, C. Luo, and C. S. Zender (2010), Impacts of atmospheric nutrient inputs on marine biogeochemistry, *J Geophys Res-Bioge*, 115, G01006, doi:01010.01029/02009jg001115, doi: 10.1029/2009jg001115.

Krishnamurthy, A., J. K. Moore, N. Mahowald, C. Luo, S. C. Doney, K. Lindsay, and C. S. Zender (2009), Impacts of increasing anthropogenic soluble iron and nitrogen deposition on ocean biogeochemistry, *Global Biogeochem Cy*, 23, doi: Doi 10.1029/2008gb003440.

Krom, M. D., K. C. Emeis, and P. Van Cappellen (2010), Why is the Eastern Mediterranean phosphorus limited?, *Prog Oceanogr*, 85(3-4), 236-244, doi: DOI 10.1016/j.pocean.2010.03.003.

Krupke, A., W. Mohr, J. LaRoche, B. M. Fuchs, R. I. Amann, and M. M. M. Kuypers (2015), The effect of nutrients on carbon and nitrogen fixation by the UCYN-A-haptophyte symbiosis, *Isme J*, 9(7), 1635-1647, doi: 10.1038/ismej.2014.253.

Kustka, A., S. Sanudo-Wilhelmy, E. J. Carpenter, D. G. Capone, and J. A. Raven (2003), A revised estimate of the iron use efficiency of nitrogen fixation, with special reference to the marine cyanobacterium *Trichodesmium* spp. (Cyanophyta), *Journal of Phycology*, 39(1), 12-25

Lamarque, J. F., et al. (2013), Multi-model mean nitrogen and sulfur deposition from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): evaluation of historical and projected future changes, *Atmos Chem Phys*, 13(16), 7997-8018, doi: 10.5194/acp-13-7997-2013.

Landolfi, A., H. Dietze, W. Koeve, and A. Oschlies (2013), Overlooked runaway feedback in the marine nitrogen cycle: the vicious cycle, *Biogeosciences*, 10(3), 1351-1363, doi: 10.5194/bg-10-1351-2013.

Landolfi, A., W. Koeve, H. Dietze, P. Kähler, and A. Oschlies (2015), A new perspective on environmental controls of marine nitrogen fixation, *Geophys Res Lett*, 42(11), 4482-4489, doi: 10.1002/2015GL063756.

Laws, E. A., P. G. Falkowski, W. O. Smith, H. Ducklow, and J. J. McCarthy (2000), Temperature effects on export production in the open ocean, *Global Biogeochem Cy*, 14(4), 1231-1246, doi: 10.1029/1999GB001229.

Le Quere, C., et al. (2005), Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models, *Global Change Biol*, 11(11), 2016-2040, doi: DOI 10.1111/j.1365-2468.2005.01004.x.

Le Quere, C., et al. (2016), Role of zooplankton dynamics for Southern Ocean phytoplankton biomass and global biogeochemical cycles, *Biogeosciences*, 13(14), 4111-4133, doi: 10.5194/bg-13-4111-2016.

Lesworth, T., A. R. Baker, and T. Jickells (2010), Aerosol organic nitrogen over the remote Atlantic Ocean, *Atmos Environ*, 44(15), 1887-1893, doi: DOI 10.1016/j.atmosenv.2010.02.021.

Letscher, R. T., D. A. Hansell, D. Kadko, and N. R. Bates (2013), Dissolved organic nitrogen dynamics in the Arctic Ocean, *Mar Chem*, 148, 1-9, doi: dx.doi.org/10.1016/j.marchem.2012.10.002.

Letscher, R. T., J. K. Moore, Y. C. Teng, and F. Primeau (2015), Variable C: N: P stoichiometry of dissolved organic matter cycling in the Community Earth System Model, *Biogeosciences*, 12(1), 209-221, doi: 10.5194/bg-12-209-2015.

Liu, X. J., et al. (2013), Enhanced nitrogen deposition over China, *Nature*, 494(7438), 459-462, doi: Doi 10.1038/Nature11917.

Lønborg, C., and X. A. Álvarez-Salgado (2012), Recycling versus export of bioavailable dissolved organic matter in the coastal ocean and efficiency of the continental shelf pump, *Global Biogeochem Cy*, 26(3), n/a-n/a, doi: 10.1029/2012GB004353.

Loscher, C. R., A. Kock, M. Konneke, J. LaRoche, H. W. Bange, and R. A. Schmitz (2012), Production of oceanic nitrous oxide by ammonia-oxidizing archaea, *Biogeosciences*, 9(7), 2419-2429, doi: 10.5194/bg-12-209-2015.

Luo, Y. W., et al. (2012), Database of diazotrophs in global ocean: abundance, biomass and nitrogen fixation rates, *Earth Syst. Sci. Data*, 4(1), 47-73, doi: 10.5194/essd-4-47-2012.

Mahaffey, C., A. F. Michaels, and D. G. Capone (2005), The conundrum of marine N₂ fixation, *Am J Sci*, 305(6-8), 546-595, doi: DOI 10.2475/ajs.305.6-8.546.

Martino, M., D. Hamilton, A. R. Baker, T. D. Jickells, T. Bromley, Y. Nojiri, B. Quack, and P. W. Boyd (2014), Western Pacific atmospheric nutrient deposition fluxes, their impact on surface ocean productivity, *Global Biogeochem Cy*, 28(7), 712-728, doi: Doi 10.1002/2013gb004794.

Martiny, A. C., C. T. A. Pham, F. W. Primeau, J. A. Vrugt, J. K. Moore, S. A. Levin, and M. W. Lomas (2013), Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter, *Nature Geosci*, 6(4), 279-283, doi: 10.1038/ngeo1757.

Meyer, J., C. R. Löscher, S. C. Neulinger, A. F. Reichel, A. Loginova, C. Borchard, R. A. Schmitz, H. Hauss, R. Kiko, and U. Riebesell (2016), Changing nutrient stoichiometry affects phytoplankton production, DOP accumulation and dinitrogen fixation – a mesocosm experiment in the eastern tropical North Atlantic, *Biogeosciences*, 13(3), 781-794, doi: 10.5194/bg-13-781-2016.

Michaels, A. F., D. A. Siegel, R. J. Johnson, A. H. Knap, and J. N. Galloway (1993), Episodic Inputs of Atmospheric Nitrogen to the Sargasso Sea - Contributions to New Production and Phytoplankton Blooms, *Global Biogeochem Cy*, 7(2), 339-351, doi: Doi 10.1029/93gb00178.

Mills, M. M., and K. R. Arrigo (2010), Magnitude of oceanic nitrogen fixation influenced by the nutrient uptake ratio of phytoplankton, *Nat Geosci*, 3, 412-416, doi: 10.1038/ngeo856.

Moore, C. M., et al. (2009), Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability, *Nat Geosci*, 2(12), 867-871, doi: Doi 10.1038/Ngeo667.

Moore, C. M., et al. (2013), Processes and patterns of oceanic nutrient limitation, *Nat Geosci*, 6(9), 701-710, doi: Doi 10.1038/Ngeo1765.

Moore, J. K., and S. C. Doney (2007), Iron availability limits the ocean nitrogen inventory stabilizing feedbacks between marine denitrification and nitrogen fixation, *Global Biogeochem Cy*, 21(2), doi: Doi 10.1029/2006gb002762.

Moore, J. K., S. C. Doney, K. Lindsay, N. Mahowald, and A. F. Michaels (2006), Nitrogen fixation amplifies the ocean biogeochemical response to decadal timescale variations in mineral dust deposition, *Tellus B*, 58(5), 560-572, doi: DOI 10.1111/j.1600-0889.2006.00209.x.

Muller-Karger, F. E., R. Varela, R. Thunell, R. Luerssen, C. M. Hu, and J. J. Walsh (2005), The importance of continental margins in the global carbon cycle, *Geophys Res Lett*, 32(1), doi: 10.1029/2004GL021346.

Naqvi, S. W. A., H. W. Bange, L. Farias, P. M. S. Monteiro, M. I. Scranton, and J. Zhang (2010), Marine hypoxia/anoxia as a source of CH₄ and N₂O, *Biogeosciences*, 7(7), 2159-2190, doi: 10.5194/bg-7-2159-2010.

Okin, G. S., et al. (2011), Impacts of atmospheric nutrient deposition on marine productivity: Roles of nitrogen, phosphorus, and iron, *Global Biogeochem Cy*, 25, doi: Doi 10.1029/2010gb003858.

Rockstrom, J., et al. (2009), A safe operating space for humanity, *Nature*, 461(7263), 472-475, doi: 10.1038/461472a.

Santoro, A. E., C. Buchwald, M. R. McIlvin, and K. L. Casciotti (2011), Isotopic Signature of N₂O Produced by Marine Ammonia-Oxidizing Archaea, *Science*, 333(6047), 1282-1285, doi: 10.1126/science.1208239

Seitzinger, S. P., J. A. Harrison, E. Dumont, A. H. W. Beusen, and A. F. Bouwman (2005), Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, *Global Biogeochem Cy*, 19(4), GB4S01, 10.1029/2005GB002606

Seitzinger, S. P., J. A. Harrison, J. K. Bohlke, A. F. Bouwman, R. Lowrance, B. Peterson, C. Tobias, and G. Van Drecht (2006), Denitrification across landscapes and waterscapes: A synthesis, *Ecol Appl*, 16(6), 2064-2090

Seitzinger, S. P., et al. (2010), Global river nutrient export: A scenario analysis of past and future trends, *Global Biogeochem Cy*, 24, doi: Doi 10.1029/2009gb003587.

Sharples, J., J. J. Middelburg, K. Fennel, and T. D. Jickells (2016), What proportion of riverine nutrients reaches the open ocean?, *Global Biogeochem Cy*, n/a-n/a, doi: 10.1002/2016GB005483.

Singh, A., N. Gandhi, and R. Ramesh (2012), Contribution of atmospheric nitrogen deposition to new production in the nitrogen limited photic zone of the northern Indian Ocean, *J Geophys Res-Oceans*, 117, C06004, doi:06010.01029/02011jc007737, doi: 10.1029/2011jc007737.

Singh, A., M. W. Lomas, and N. R. Bates (2013), Revisiting N-2 fixation in the North Atlantic Ocean: Significance of deviations from the Redfield Ratio, atmospheric deposition and climate variability, *Deep-Sea Res Pt II*, 93, 148-158, doi: 10.1016/j.dsr2.2103.04.008.

Singh, A., S. E. Baer, U. Riebesell, A. C. Martiny, and M. W. Lomas (2015), C : N : P stoichiometry at the Bermuda Atlantic Time-series Study station in the North Atlantic Ocean, *Biogeosciences*, 12(21), 6389-6403, doi: 10.5194/bg-12-6389-2015.

Slattery, M. C., and J. D. Phillips (2011), Controls on sediment delivery in coastal plain rivers, *J Environ Manage*, 92(2), 284-289, doi: 10.1016/j.jenvman.2009.08.022.

Sohm, J. A., E. A. Webb, and D. G. Capone (2011), Emerging patterns of marine nitrogen fixation, *Nat. Rev. Microbiol.*, 9(7), 499-508, doi: 10.1038/nrmicro2594.

Somes, C. J., and A. Oschlies (2015), On the influence of "non-Redfield" dissolved organic nutrient dynamics on the spatial distribution of N-2 fixation and the size of the marine fixed nitrogen inventory, *Global Biogeochem Cy*, 29(7), 973-993, doi: 10.1002/2014GB005050.

Somes, C. J., A. Oschlies, and A. Schmittner (2013), Isotopic constraints on the pre-industrial oceanic nitrogen budget, *Biogeosciences*, 10(9), 5889-5910, doi: 10.5194/bg-10-5889-2013.

Somes, C. J., A. Landolfi, W. Koeve, and A. Oschlies (2016), Limited impact of atmospheric nitrogen deposition on marine productivity due to biogeochemical feedbacks in a global ocean model, *Geophys Res Lett*, 43(9), 4500-4509, doi: 10.1002/2016GL068335.

Spokes, L. J., S. G. Yeatman, S. E. Cornell, and T. D. Jickells (2000), Nitrogen deposition to the eastern Atlantic Ocean. The importance of south-easterly flow, *Tellus B*, 52(1), 37-49, doi: DOI 10.1034/j.1600-0889.2000.00062.x.

Srinivas, B., and M. M. Sarin (2013), Atmospheric dry-deposition of mineral dust and anthropogenic trace metals to the Bay of Bengal, *J Marine Syst*, 126, 56-68, doi: 10.1016/j.jmarsys.2012.11.004.

Straub, M., D. M. Sigman, H. J. Ren, A. Martinez-Garcia, A. N. Meckler, M. P. Hain, and G. H. Haug (2013), Changes in North Atlantic nitrogen fixation controlled by ocean circulation, *Nature*, 501(7466), 200-+, doi: Doi 10.1038/Nature12397.

Sundarambal, P., R. Balasubramanian, P. Tkalic, and J. He (2010), Impact of biomass burning on ocean water quality in Southeast Asia through atmospheric deposition: field observations, *Atmos Chem Phys*, 10(23), 11323-11336, doi: 10.5194/acp-10-11323-2010.

Suntharalingam, P., E. Buitenhuis, C. Le Quere, F. Dentener, C. Nevison, J. H. Butler, H. W. Bange, and G. Forster (2012), Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide, *Geophys Res Lett*, 39, doi: 10.1029/2011gl050778.

Suthhof, A., V. Ittekkot, and B. Gaye-Haake (2001), Millennial-scale oscillation of denitrification intensity in the Arabian Sea during the late Quaternary and its potential influence on atmospheric N₂O and global climate, *Global Biogeochem Cy*, 15(3), 637-649, doi: 10.1029/2000GB001337.

Syvitski, J. P. M., C. J. Vorosmarty, A. J. Kettner, and P. Green (2005), Impact of humans on the flux of terrestrial sediment to the global coastal ocean, *Science*, 308(5720), 376-380.

Tsigaridis, K., et al. (2014), The AeroCom evaluation and intercomparison of organic aerosol in global models, *Atmos Chem Phys*, 14(19), 10845-10895.

Vet, R., et al. (2014), A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus, *Atmos Environ*, 93, 3-100, doi: 10.1016/j.atmosenv.2013.10060.

Voss, M., H. W. Bange, J. W. Dippner, J. J. Middelburg, J. P. Montoya, and B. Ward (2013), The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change, *Philos T R Soc B*, 368(1621), doi: 10.1098/rstb.2013.0121.

Ward, B. A., S. Dutkiewicz, C. M. Moore, and M. J. Follows (2013), Iron, phosphorus, and nitrogen supply ratios define the biogeography of nitrogen fixation *Limnol. Oceanogr.*, 58(6), 2059-2075, doi: 10.4319/lno.2013.58.6.2059.

Weber, R. J., H. Guo, A. G. Russell, and A. Nenes (2016), High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, *Nature Geosci, advance online publication*, doi: 10.1038/ngeo2665.

Weber, T. S., and C. Deutsch (2010), Ocean nutrient ratios governed by plankton biogeography, *Nature*, 467(7315), 550-554, doi: 10.1038/nature09403.

Yang, S., and N. Gruber (2016), The anthropogenic perturbation of the marine nitrogen cycle by atmospheric deposition: Nitrogen cycle feedbacks and the 15N Haber-Bosch effect, *Global Biogeochem Cy*, 30(10), 1418-1440, doi: 10.1002/2016GB005421.

Zamora, L. M., and A. Oschlies (2014), Surface nitrification: A major uncertainty in marine N₂O emissions, *Geophys Res Lett*, 41(12), 4247-4253, doi: 10.1002/2014GL060556.

Zamora, L. M., J. M. Prospero, and D. A. Hansell (2011), Organic nitrogen in aerosols and precipitation at Barbados and Miami: Implications regarding sources, transport and deposition to the western subtropical North Atlantic, *J Geophys Res*, 116, D20309, doi:10.1029/2011JD015660, doi: 10.1029/2011JD015660.

Zamora, L. M., A. Landolfi, A. Oschlies, D. A. Hansell, H. Dietze, and F. Dentener (2010), Atmospheric deposition of nutrients and excess N formation in the North Atlantic, *Biogeosciences*, 7(2), 777-793, doi: 10.5194/bg-7-777-2010.